

-5- BASIC DOC.-

C03C1/00

⑪ Publication number:

0 103 448
A2



Office européen des brevets

⑫

EUROPEAN PATENT APPLICATION

⑰ Application number: 83305120.4

⑤ Int. Cl.: C 03 C 3/04, C 03 C 13/00,
C 03 C 1/00, C 04 B 35/00

⑱ Date of filing: 05.09.83

③① Priority: 15.09.82 US 418215

⑦① Applicant: Corning Glass Works, Houghton Park,
Corning, New York, 14831 (US)

④③ Date of publication of application: 21.03.84
Bulletin 84/12

⑦② Inventor: Miller, Stephen Bruce, 67 West Fourth Street,
Corning New York 14830 (US)
Inventor: Stewart, Ronald Leroy, 741 Cardinal Lane, Big
Flats New York (US)
Inventor: Thompson, David Allen, 1259 Stoneybrook
Drive, Horseheads New York (US)

⑧④ Designated Contracting States: AT BE CH DE FR GB IT
LI NL SE

⑦④ Representative: Kyle, Diana et al, ELKINGTON AND FIFE
High Holborn House 52/54 High Holborn, London
WC1V 6SH (GB)

⑤④ Production of sintered glasses and ceramics.

⑤⑦ A process for the production of a glass or ceramic article comprising a vapour phase oxidation wherein vaporized compounds are oxidized to form particulate oxide soot which is captured and consolidated to a unitary article by sintering, characterised in that at least one of the compounds is a β -diketonate complex of a metal selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table is disclosed.

A process for the production of a glass optical waveguide comprising a vapour phase oxidation wherein compounds of selected metals are vaporized, the vapours are transported to an oxidation site, the vapours are oxidized at the site to form particulate metal oxide soot, the soot is captured and consolidated into clear glass and the glass is drawn into optical waveguide fibre, characterised in that at least one of the compounds is a β -diketonate complex of a metal selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table is also disclosed.

The present invention offers advantages over the prior art.

"Production of Sintered Glasses and Ceramics"

This invention relates to the production of sintered glasses and ceramics; more particularly, it relates to the production of pure glass or ceramic products by vapour deposition and subsequent sintering.

5 The favoured commercial practice in the production of very pure glass products, such as glass optical waveguides, is by vapour deposition. The process conventionally involves the transport of vaporized reactants to an oxidation site, e.g. a burner or hot plasma zone, adjacent to a deposition substrate or within a glass deposition tube, oxidation of the reactants at the oxidation site to form a particulate oxide or soot oxidation product on the mandrel or tube and processing of the deposited soot to convert it to clear glass.

10 The vaporization characteristics of the reactants are critical for such processing. In commercial practice, these reactants have consisted of the volatile halides or hydrides of the selected metals or metalloids, e.g. the halides or oxyhalides of silicon, phosphorus, germanium and boron. These compounds have high vapour pressures at temperatures which are easy to maintain in a vapour delivery system and are converted to pure oxides at the oxidation site. In some cases, systems which operate at temperatures above the boiling temperature of the volatile halide or oxyhalide compound at atmospheric pressure have been used.

25 Suggestions have been made that other volatile compounds of these metals, such as the organometallic compounds, could be used, but there has been no commercial application of this proposal in the waveguide field. GB 2,071,644 suggests that silanes, chloro- and alkyl-substituted silanes and/or silicate

30

-2-

esters may be used in vapour delivery systems for optical waveguide production, but, in general, the instability, high reactivity and/or limited vapour pressures of such compounds have mitigated against the use thereof.

It has been recognized that it would be desirable to use many of the common glass modifying oxides, such as MgO , Na_2O , Al_2O_3 and CaO , in the fabrication of glass optical waveguide by vapour deposition techniques, but no satisfactory technique for incorporating these oxides in vapour-deposited glass has yet been developed. Most of the main group and rare earth metals useful as modifiers in transparent glasses do not form volatile chlorides or other volatile, but stable inorganic compounds. Thus, although they have potential utility as modifying dopants in glass waveguides, no successful technique for incorporating these oxides in vapour-deposited glass in high purity and with close control over concentration has been developed.

Proposals have been made to use metal alkyls as metal sources for the vapour deposition of oxides, but these compounds are generally so unstable as to be hazardous. For example, the compounds trimethylaluminum, $\text{Al}(\text{CH}_3)_3$, and dimethylzinc, $\text{Zn}(\text{CH}_3)_2$, are volatile and reactive, but are pyrophoric and thus very dangerous to store and to use.

U.S. Patent No. 3,801,294 discloses an early approach to the incorporation of main group modifiers in vapour-deposited oxide glasses wherein direct vaporization of metal halides from the solid state is proposed. This approach is disadvantageous because high delivery system temperatures must be maintained to achieve even moderate vapour pressures, and it is

-3-

difficult to control the concentrations of dopants present in the carrier gas stream.

U.S. Patent No. 3,883,336 proposed an alternative approach for incorporating main group oxides in vapour-deposited glass wherein a solution containing a soluble salt of the desired metal is nebulized and the dispersed solution directed into an oxidation flame wherein metal oxide soot is generated. Unlike solvent-free vapour phase oxidation, this approach does not reproducibly provide an oxide soot having a particle size distribution such that it may be sintered into a void-free homogeneous mixed-oxide glass or ceramic. Moreover, the solvents used are potential sources of contamination in the product. Neither particulate oxide inclusions nor contaminating

impurities may be tolerated in optical waveguide glass.

U.S. Patent Nos. 4,141,710 and 4,173,459 suggest an alternative technique for using solutions wherein a solvent carrying a thermally decomposable organic or inorganic compound of the desired metal is supplied to the inner surface of a bait tube or crucible. This process is one of thermal decomposition, rather than vapour phase oxidation, and is therefore not well suited to the fabrication of glass optical waveguides. The deposits produced by hot-surface thermal decomposition again differ significantly in morphology from the soots produced by vapour phase oxidation and often exhibit cracking and flaking if thick. Consequently, such deposits may be very difficult to convert to defect-free glass. Thus, while the thermal decomposition of inorganic and organometallic compounds, including metal chelates, such as the acetylacetonates, has been used to produce thin oxide films on glass sheet (G.B. 1,454,378 and G.B. 2,033,374A), and for metal plating (U.S. 3,356,527 and U.S. 3,049,797), such practices are not commercially adaptable to the

fabrication of bulk glass products, such as optical waveguides.

It is therefore an object of the present invention to provide a process for the production
5 of glass or other pure ceramic products which permits the incorporation of main group and rare earth-metal oxides into such products without undesirable voids or compositional discontinuities, such as particulate oxide inclusions.

10 It is a further object of the present invention to provide a process for fabricating glass optical waveguides incorporating such metal oxides as dopants wherein good control over the concentration of dopants in the vapour-deposited glass and high purity in the
15 vapour deposition product may be achieved.

The present invention involves the use of selected vaporizable chelates of selected main group and rare earth metals as vapour sources for the production of pure glass and ceramic products by
20 the consolidation of oxide soot produced by vapour phase oxidation. The process follows that presently used for the deposition of pure oxide glass-formers and glass-modifiers for products, such as optical waveguides, in that the metal compounds are vaporized
25 and transported as vapour to an oxidation site where the compounds are reacted in the vapour phase to form finely divided soot. In current practice, this oxide soot is then captured and consolidated by heating to produce clear glass which may ultimately be formed
30 into a product, such as an optical waveguide fibre. Such vapour deposition processes are advantageous because they permit the fabrication of very pure glass or ceramic products, i.e. products made of amorphous or crystalline materials incorporating not
35 more than 0.01%, by weight, total of metallic impurities.

-5-

Metals which may be transported in accordance with the present invention may be selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of elements of the Periodic Table. These are provided as preparations of stable metal chelate compounds which may be vaporized at moderate temperatures and transported at substantial partial pressures. The transported chelate vapours are converted by vapour phase reaction at the reaction site to finely divided oxide soot having particle sizes and a particle size distribution suitable for capture and consolidation into a unitary or monolithic product, preferably a clear glass. The metal chelates used in the process are selected metal β -diketonates, i.e. complexes of the metal with one or more β -diketonate ligands derived from the class of diketones known as β -diketones. The β -diketonate complex may include diketonate ligands only, or additional ligands may be present in the complex as adducts to the metal chelate structure.

Compounds selected from this group are liquids or solids at ambient temperatures and pressures. They are relatively stable against oxidation in air, yet may exhibit vapour pressures of over 10 mm Hg (13.34 millibars) and frequently over 100 mm Hg (133.4 millibars) at temperatures below the decomposition temperatures thereof. The selected compounds exhibit sufficient stability to be transported at these temperatures without significant decomposition, yet are readily reacted in the vapour phase to form pure metal oxides in the presence of oxygen at the reaction site, with or without additional heating depending upon the particular vapour phase reaction induced.

Utilizing these compounds, main group and rare earth elements may be transported in vapour form to a

-6-

reaction site in substantial, but controllable concentrations without the use of a solvent carrier, so that high purity oxides of these metals in very finely-divided form suitable for sintering to clear glasses or fine-grained ceramics may be provided.

The present invention is illustrated by the accompanying drawings wherein:

Fig. 1 illustrates thermogravimetric curves for selected β -diketonate compounds suitable for use in accordance with the present invention;

Fig. 2 illustrates vapour pressure data for selected β -diketonate compounds suitable for use in accordance with the present invention;

Fig. 3 illustrates thermogravimetric curves showing the effects of adduct variation on the volatility of some adducted β -diketonate compounds; and

Fig. 4 illustrates an electron photomicrograph of a captured metal oxide soot provided in accordance with the present invention.

Oxides to be deposited by vapour phase oxidation in accordance with the present invention include the oxides of metals selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA and IVB of the Periodic Table. These may include oxides capable of forming glasses, e.g. aluminium oxide, but are predominantly oxides used as intermediates or modifiers in glass-forming systems, e.g. the alkali and alkaline earth metal oxides. Examples of candidate metals are as follows: Group IA - Li, Na; Group IB - Cu; Group IIA - Be, Mg; Group IIB - Zn, Cd, Hg; Group IIIB - Sc, Y; Group IIIA - Al, Ga; Group IVA - Sn; and Group IVB - Zr, Hf.

Rare earth metal oxides may also be deposited by vapour phase oxidation in accordance with the present invention. An example of a rare earth metal oxide which may be advantageously used as a dopant in optical wave-

guide glass is CeO_2 , which in trace amounts may improve the resistance of waveguides to radiation damage. Other rare earth oxides which have been considered for use as glass modifiers in fused silica waveguides are La and Yb.

5 To be suitable for use in a vapour delivery system for vapour phase reaction, compounds of metals selected for incorporation in the deposited oxide must have a significant vapour pressure at some temperature below the compound's decomposition temperature.. This vapour
10 pressure requirement varies depending upon both the concentration of metal oxide needed in the deposition product and the deposition rate desired, but may range from as little as 1 mm Hg (1.334 millibars) for a compound needed in only trace amounts to a vapour pressure
15 of at least 10 mm Hg (13.34 millibars), preferably at least 100 mm Hg (133.4 millibars) for compounds to be incorporated as major intermediate or glass-modifying constituents of the deposited glass.

 The structure of the metal β -diketonate molecule
20 is known to consist of a metal atom surrounded by β -diketone ligands corresponding to the general formula: $[\text{R-CO-CH-CO-R'}]^-$. The R and R' constituents are typically alkyl or fluorinated alkyl groups containing from 1 to 4 carbon atoms. It is known that, for a given metal, the
25 volatility of the corresponding metal β -diketonate depends strongly on the identity of the R and R' constituents.

 Unsubstituted, low molecular weight diketones, such as acetylacetone (2,4-pentane-dione), have been used to form soluble metal complexes for the formation of metal
30 oxide films by thermal decomposition on heated substrates. However, metal β -diketonates incorporating these ligands do not generally exhibit sufficient vapour pressures below the decomposition temperatures thereof to be useful vapour sources for the formation of main group metal
35 oxides by vapour phase oxidation according to the present

invention.

In contrast, metal β -diketonates wherein the β -diketone ligands are of higher formula weight (i.e. at least 153) and particularly wherein they are derived from fluorinated diketones, may exhibit significantly higher vapour pressures, and thus may be used to generate significant volumes of metal-containing vapours for the vapour phase generation of oxide soot. It has been theorized that the enhanced volatility of fluorine-substituted β -diketonate complexes is due to an effect on the van der Waals forces among chelate molecules caused by the high electronegativity of fluorine (R.E. Sievers, et al., Science, 201, [4352], pp 217-223). For large fluorine-free ligands, steric hindrance may be a factor.

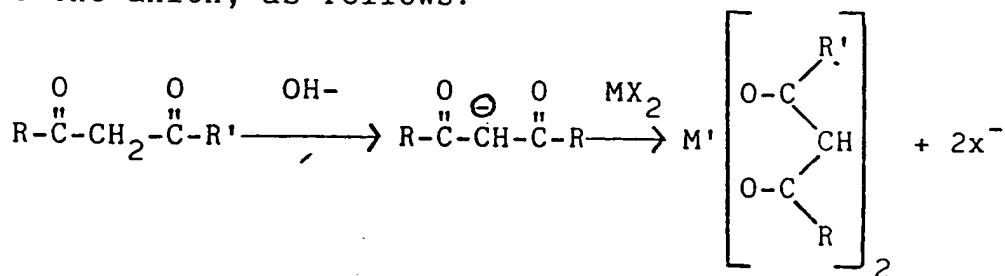
Examples of fluorinated and/or high molecular weight β -diketones suitable for complexing with main group or rare earth metals to form volatile metal chelates are reported in Table 1 below. Included in Table 1 for each named compound are a molecular structure for each compound, a symbol or trivial name used as a shorthand notation for the compounds in subsequent Examples and boiling temperatures for each compound (reported at 760 mm Hg (1.01 bar), except where otherwise indicated). The H prefix in each of the shorthand notations (e.g. Hhfa) refers to the neutral compound in diketone form, while the diketonate anion form is written without the prefix, (hfa)⁻.

Table 1
Structures and Properties of β -diketones Used as Ligands

Compound	Structure	Trivial Name (Symbol)	Boiling Point
1,1,1-trifluoro-2,4-pentane-dione	$\begin{array}{c} \text{O} \\ \parallel \\ \text{F}_3\text{C}-\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}-\text{C}-\text{CH}_3 \end{array}$	trifluoroacetylacetone (Htfa)	B.P. = 107°C
1,1,1,5,5,5-hexafluoro-2,4-pentane-dione	$\begin{array}{c} \text{O} \\ \parallel \\ \text{F}_3\text{C}-\overset{\text{O}}{\parallel}-\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}-\text{C}-\text{CF}_3 \end{array}$	hexafluoroacetylacetone (Hhfa)	B.P. = 70°C
2,2,6,6-tetramethyl-3,5-heptane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ (\text{H}_3\text{C})_3\text{C}-\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}-\text{C}(\text{CH}_3)_3 \end{array}$	(Hthd) or (Hdpm)	B.P. = 214-216°
6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ (\text{H}_3\text{C})_3\text{C}-\overset{\text{O}}{\parallel}-\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}-\text{C}(\text{CF}_2)_2-\text{CF}_3 \end{array}$	(Hfod)	B.P. = 33°
2,2,7-trimethyl-3,5-octane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ (\text{H}_3\text{C})_3\text{C}-\overset{\text{O}}{\parallel}-\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}-\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)_2 \end{array}$	(Htod)	B.P. = 55°C (0.1 mm. Hg/ 0.1334 mb)
1,1,1,5,5,6,6,7,7-decafluoro-2,4-heptane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{F}_3\text{C}-\overset{\text{O}}{\parallel}-\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}-\text{C}-\text{CF}_2-\text{CF}_2-\text{CF}_3 \end{array}$	(Hdfhd)	B.P. = 99-105°C
1,1,1-trifluoro-6-methyl-2,4-heptane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{F}_3\text{C}-\overset{\text{O}}{\parallel}-\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}-\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)_2 \end{array}$	(Htfmhd)	

Because of the practical requirement of high volatility, the use of the fluorinated β -diketonates of the main group and rare earth metals constitutes the preferred procedure for the vapour phase reaction of main group metals in accordance with the present invention and the use of one or more of the fluorinated ligands from Table 1 above is particularly preferred.

The mechanism of bonding in β -diketonate complexes is almost always through the oxygen atoms of the ligand, after deprotonation of the diketone to give the anion, as follows:



As is well known, the charge on the diketonate anion is actually delocalized about the $-\text{CO}-\text{CH}-\text{CO}-$ functional group, rather than at the central carbon atom as shown.

β -diketonate complexes usually exhibit high solubility in non-polar organic solvents, e.g. hexane or carbon tetra-chloride, with much lower solubility in alcohols or water. The production of these complexes has been described in the literature. See, for example, "Metal β -Diketonates and Allied Derivatives", R.C. Mehrotra, R. Bohra and B.P. Gaur, Academic Press, New York, (1978).

Examples of specific β -diketonate complexes of metals which should exhibit vapour pressures of at least 10 mm Hg (13.34 millibars) without significant decomposition at temperatures of 250°C or below and thus should be suitable sources of those metals for reaction by vapour phase oxidation to provide metal oxides, are

indicated in Table 2 below. Table 2 includes a listing of the metals as elements, together with an indication of which ligands are suitable for complexing therewith, the latter being identified by commonly used symbols as reported in Table 1 above.

Table 2

Volatile β -Diketonate Complexes

	<u>Elements</u>	<u>Ligands</u>				
		<u>(tfa)⁻</u>	<u>(hfa)⁻</u>	<u>(thd)⁻</u>	<u>(dfhd)⁻</u>	<u>(fod)⁻</u>
10	Li			X		
	Na			X		
	Be	X	X			
	Mg		X		X	
	Sc	X		X		
15	Y			X		X
	Cu	X	X			X
	Hf					X
	Ti		X			
	Zr		X			
20	Zn	X	X	X		
	Cd		X			
	Al	X	X			X
	Ga	X	X			
	Ce					X
25						

Where only minor concentrations of a selected oxide are to be incorporated in a soot product, vapour pressures as high as 10 mm Hg (13.34 millibars) may not be required and pressures as low as 1 mm Hg (1.334 millibars) may provide sufficient metal vapour concentrations. An example of such a case is the incorporation of cerium oxide as a trace dopant to suppress radiation discolouration in a silicate core glass for an optical waveguide, where concentrations exceeding 0.1% CeO₂, by weight, are rarely needed. Ce(tod)₄ is an example of

a rare earth metal β -diketonate which, while not demonstrating a vapour pressure as high as some of the above-described fluorinated β -diketonates exhibits sufficient vapour pressure to constitute a
5 suitable vapour source for generating a small concentration of cerium oxide by vapour phase oxidation. Of course, even for trace doping, a more convenient practice would be to use a higher vapour pressure complex, such as $\text{Ce}(\text{fod})_4$, where
10 such is available.

In many cases, β -diketonate complexes tend to form adducts with solvent molecules used in preparation, particularly when the complex is not coordinatively saturated and the solvent is a good Lewis
15 base. The resulting adducted β -diketonate complexes may be quite stable and may themselves exhibit sufficient stability and volatility to constitute useful vapour sources. Examples of compounds which form adducts with β -diketonates are ammonia, water, pyridine, bipyridyl,
20 phenanthroline, tetrahydrofuran and dimethylformamide. These attach to the complex as additional ligands to achieve six-fold or higher coordination with the metal.

The method by which metal oxide soot is captured and consolidated to form a glass or other product,
25 after being generated by the vapour phase oxidation of β -diketonate complexes in accordance with the present invention, is not critical. Prior art soot processing techniques may be used, including capturing the soot on a suitable mandrel or bait rod, capturing the
30 soot in a collection container, consolidating the captured soot by sintering on or off the bait or after shaping the loose soot by compaction or slipcasting and treating the captured soot prior to or during consolidation to remove non-metallic impurities, such
35 as water, carbon or fluorine therefrom.

-13-

The following Examples describe β -diketonate compounds which have been prepared and, based on the properties thereof, are considered suitable for use as main group metal sources for the production of pure oxides suitable for glass formation by vapour phase oxidation processes.

Example 1 - Al(hfa)_3

A β -diketonate complex of aluminium (a Group IIIA metal) is prepared by reacting hexafluoroacetylacetone (Hhfa) with aluminium chloride. A 1.06 g sample of AlCl_3 is added to 10 ml of CCl_4 with stirring under nitrogen. A solution of (Hhfa) in CCl_4 is slowly added to the AlCl_3 solution, with large amounts of HCl being evolved during the addition. The reaction mixture is refluxed for 30 minutes and the hot mixture is thereafter passed through a frit filter.

The clear filtrate crystallizes on cooling to give about 5.21 g of a white crystalline product. This product is purified by vacuum sublimation at 80°C into a dry ice-cooled cold trap.

Infrared spectral analysis of a sample of the product in KBr corresponds to that reported in the literature for Al(hfa)_3 . This compound sublimes readily at temperatures above 50°C , melts at about $72-74^\circ\text{C}$ and has a reported vapour pressure of about 100 mm Hg (133.4 millibars) at 125°C . This indicates that the compound would be a suitable source of aluminium-containing vapours for the production of sinterable oxide soot by a vapour phase reaction process.

Example 2 - Mg(hfa)_2

β -diketonate complexes of the Group IIA metal magnesium are prepared by reacting (Hhfa) with basic magnesium carbonate. A 2.5 g sample of basic magnesium carbonate, $4 \text{ MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot n\text{H}_2\text{O}$ ($n \approx 6$), is suspended

-14-

in 100 ml of ether with stirring under nitrogen.

A 10.41 g sample of (Hhfa) is added to the suspension and the mixture is refluxed for 2 hours. The ether is then separated from a solid residual phase by

5 decantation and evaporated to dryness. Evaporation leaves a residual white powder product identified as the ether-water adduct of magnesium hexafluoro-acetylacetonate, $\text{Mg(hfa)}_2 \cdot 1.5\text{Et}_2\text{O} \cdot \text{H}_2\text{O}$. This adducted complex melts at about 225°C and may be vaporized by
10 sublimation at 165°C.

To prepare a tetrahydrofuran (THF) adduct of Mg(hfa)_2 , a 20 ml volume of THF is added to the ether-water adduct produced as described above and the resulting solution is stirred for 18 hours.

15 Rotary evaporation of the solution leaves a white powder residue identified by proton nuclear magnetic resonance (nmr) as $\text{Mg(hfa)}_2 \cdot 4\text{THF}$. Sublimation of this compound to a dry ice-cooled cold trap produces the adduct $\text{Mg(hfa)}_2 \cdot 2\text{THF}$, a compound having a melting
20 point of approximately 130°C which may be vaporized at 160°C to generate Mg-containing vapours for a vapour phase oxidation process.

Example 3 - Na (tfmhd)

A β -diketonate complex of the Group IA metal
25 sodium is prepared by reacting sodium hydroxide with a beta-diketone containing a 7-carbon chain. A 4.08 g sample of pelletized NaOH is dissolved in 50 ml of water in a separatory funnel and 20.0 g of the diketone 1,1,1-trifluoro-6-methyl-2,4-heptane-dione (Htfmhd)
30 is added to the solution. This mixture is shaken periodically over a 15-minute interval and then ether is added to extract the Na- β -diketonate product from the mixture. The pale yellow ether extract is evaporated to dryness in air giving a pale yellow solid
35 identified as Na(tfmhd), having an undetermined melting

-15-

point, but giving evidence of sublimation at about 260°C with some evidence of thermal decomposition.

Example 4 - Ce(fod)₄

5 A β-diketonate complex of the rare earth metal cerium is prepared by reacting cerium nitrate with 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione.

10 A 68.2 g sample of this β-diketone (Hfod) is added to 115 ml of 2M aqueous NH₄OH, resulting in a white precipitate which is separated and dissolved in 200 ml of water and 200 ml of methanol. The resulting solution is placed in an addition funnel and added dropwise to a nitric acid solution of cerium nitrate
15 consisting of 25.0 g Ce(NO₃)₃·6H₂O dissolved in 60 ml of 1.4 M HNO₃. 2M NH₄OH is then added to achieve and maintain pH 6.

20 The resulting mixture separates into a red oil phase and an aqueous phase. The separated mixture is stirred under O₂ at room temperature until oxidation of Ce³⁺ to Ce⁴⁺ is complete, in this case about 70 hours. Thereafter, 200 ml of hexanes are added and the organic layer containing the product is separated from the aqueous phase, filtered and evaporated to
25 dryness in a rotary evaporator. The product is crystallized from the red oil and examination of the proton nmr spectrum of the crystals shows substantially
- complete oxidation to Ce(fod)₄.

30 After purification by sublimation, the thus-produced Ce(fod)₄ exhibits a melting point of about 97°C and a vapour pressure approaching 10 mm Hg (13.34 millibars) at a temperature near 200°C. By virtue of this high vapour pressure, this compound would constitute a suitable source of Ce-containing vapours
35 for a vapour phase oxidation process in accordance

-16-

with the present invention.

Example 5 - $\text{Zn(hfa)}_2 \cdot 1.5 \text{ THF}$

Following the procedure reported by Chatteraj,
5 et al., J. Inorg. Nucl. Chem., 28, (1966), pages
1937-1943, the water adduct of Zn(hfa)_2 is prepared
by reacting Hhfa with zinc oxide. 10 grams of ZnO
and 35.2 ml of Hhfa are added to a flask equipped
with a condenser, magnetic stirrer and heating
10 mantel, with stirring to disperse the ZnO. 30 ml of
 H_2O is added, causing the reflux of Hhfa due to the
evolution of heat, with stirring being continued until
all evidence of reaction has ceased.

An additional 30 ml of water and 200 ml of
15 ether are then added and the mixture is refluxed for
1 hour. After cooling, excess ZnO is removed by
filtration, the ether layer is separated and dried
by adding 4\AA ($4 \times 10^{-10} \text{ m}$) molecular sieves, filtered
and the ether is then evaporated to give 55 g of
20 crude $\text{Zn(hfa)}_2 \cdot 2\text{H}_2\text{O}$ product.

Approximately 10 g of this product is dissolved
in THF at room temperature, the solvent is then
evaporated and the residue is sublimed at 150°C
under vacuum to a dry ice-cooled cold trap. Infra-red
25 spectra, nuclear magnetic resonance, thermogravimetric
analysis, elemental analysis and differential scanning
calorimetry are used to characterize this compound.
The compound is presently believed to have the chemical
formula $\text{Zn(hfa)}_2 \cdot 2\text{THF}$, with a melting temperature of
30 165°C . It exhibits excellent thermal stability, show-
ing only slight decomposition when maintained at 165°C
for about 60 hours.

Figure 1 of the accompanying drawings illustrates
the vaporization characteristics of selected β -diketon-
35 ate complexes such as reported in the above Examples,

-17-

as determined by thermogravimetric analysis. The drawing plots weight loss of a sample of the complex as a function of temperature over the heating range from 25-500°C. Temperature is plotted on the horizontal axis with the vertical axis corresponding to relative weight loss in the sample.

In general, easy vaporization without decomposition is reflected by an analysis trace exhibiting a sharp vertical drop corresponding to rapid weight loss of the heated sample in the evaporation or sublimation range, followed by a sharp horizontal trace at higher temperatures evidencing the absence of decomposable residues. The most desirable vaporization characteristics are demonstrated by Al(hfa)_3 , $\text{Zn(hfa)}_2 \cdot 2\text{THF}$ and $\text{Mg(hfa)}_2 \cdot 2\text{THF}$, which exhibit rapid and complete vaporization at temperatures in the 100-200°C range. This may be contrasted with the behaviour of a complex, such as $\text{Mg(hfa)}_2 \cdot \text{PCl}_3$, an adducted complex hereinafter described with reference to accompanying Fig. 3, which exhibits evidence of significant decomposition and incomplete volatilization even at temperatures in excess of 300°C.

Fig. 2 of the accompanying drawings illustrates vapour pressure as a function of temperature for the Al(hfa)_3 and $\text{Mg(hfa)}_2 \cdot 2\text{THF}$ β -diketonate complexes. This plot shows the very substantial vapour pressures of these two complexes, which are in the range of at least 10-100 mm Hg (13.34-133.4 millibars) at temperatures in the range of 100-200°C.

Significant variations in volatility may occur when β -diketonate compounds, such as described above, are complexed with Lewis bases to form adducted metal β -diketonates. To demonstrate some of these variations, adducts of Mg(hfa)_2 with five different Lewis bases were prepared by adding small quantities of the sublimed

-18-

ether-water adduct $Mf(hfa)_2 \cdot 1.5Et_2O \cdot H_2O$ to diethyl ether solutions of each of the six adducts: pyridine, CH_3CN , PCl_3 , dioxane and dimethyl formamide (DMF), with overnight stirring, followed by evaporation to dryness and sublimation under vacuum to obtain the products. The volatility of each of the adducts is then evaluated by thermogravimetric analysis.

Fig. 3 of the accompanying drawings illustrates thermogravimetric curves for the five different adducts $Mg(hfa)_2 \cdot xL$ wherein L represents pyridine (C_5H_5N), CH_3CN , PCl_3 , dioxane ($C_4H_8O_2$) or DMF ($(CH_3)_2NCOH$) as indicated in the drawing. The proportions x of these ligands L in the adduct molecules were not determined. A curve for $Mg(hfa)_2 \cdot 2THF$ is also included for comparison. The CH_3CN and PCl_3 adducts show evidence of decomposition, while the other adducts evaporate completely within narrow ranges of temperature, but at vaporization temperatures which vary significantly depending upon the identity of the particular adduct employed.. $Mg(hfa)_2 \cdot 2THF$ is found to be the most volatile of the various adducts tested.

The requirement that the metal compound be sufficiently volatile for efficient vaporization and vapour phase transport in accordance with the present invention arises because of the need to generate a soot product having a relatively small particle size. For example, to obtain void-free glasses by the viscous sintering of oxide soot, particle sizes not exceeding 0.1 microns (10^{-7} m) are normally preferred. The following Examples demonstrate the utility of selected volatile β -diketonate compounds for the production by vapour phase oxidation of fine, homogeneous oxide soot.

-19-

Example 6 - $\gamma\text{Al}_2\text{O}_3$

A quantity of Al(hfa)_3 produced as in Example 1 above is maintained in a liquid state in a glass
5 container by heating to about 125°C . A helium carrier gas is bubbled through the liquid Al(hfa)_3 (the latter having a vapour pressure of about 100 mm Hg (133.4 millibar) at this temperature) and the He carrier then transports vaporized Al(hfa)_3 out of the container to
10 an operating flame-oxidation burner through a heated delivery line. The flame oxidation burner is of the type described in U.S. Patent No. 4,125,288, having a design permitting the introduction of a vapour reactant stream into the burner flame via a centre orifice in
15 the burner face.

The Al(hfa)_3 is oxidized in the vapour phase in the methane-oxygen burner flame to produce a $\gamma\text{-Al}_2\text{O}_3$ soot which is collected for examination. Fig. 4 of the accompanying drawings illustrates an electron
20 photomicrograph of a sample of the $\gamma\text{-Al}_2\text{O}_3$ soot thus provided, wherein the bar corresponds to a dimension of 0.1 microns (10^{-7} m).

As is evident from a study of accompanying Fig. 4, the $\gamma\text{-Al}_2\text{O}_3$ soot produced by Al(hfa)_3 oxidation in
25 accordance with the present invention is in the form of very small (<0.1 microns/ 10^{-7} m) spherical particles, the bulk of which range from 0.025 to 0.05 microns
($\times 10^{-6}$ m) in size. This indicates that the material could readily be incorporated into ceramics or void-
30 free glasses of a desired composition by a sintering consolidation process.

Example 7 - MgO-SiO_2 Glass

A quantity of $\text{Mg(hfa)}_2 \cdot 2\text{THF}$ produced as described
35 in Example 3 above is maintained in a liquid state in a

-20-

glass container by heating to about 190°C, a temperature at which it has a vapour pressure of about 500 mm Hg (667 mb). An argon carrier gas is bubbled through this liquid at a rate of about 72 cc./min. and vaporized $\text{Mg(hfa)}_2 \cdot 2\text{THF}$ is transported by this carrier through a heated delivery line to an operating methane-oxygen burner of the type used in Example 6 above.

A second reactant stream, transported by a second delivery line and combined with the $\text{Mg(hfa)}_2 \cdot 2\text{THF}$ -carrying stream at the burner, is produced by bubbling argon at a rate of 576 cc/min through a quantity of SiCl_4 maintained at 35°C, a temperature at which SiCl_4 has a vapour pressure of 530 mm Hg (707 mb). The combined reactant stream is fed into the burner flame, that flame resulting from the combustion of 3.5 l/min. of natural gas (methane) and 3.4 l/min. of oxygen.

The SiCl_4 and $\text{Mg(hfa)}_2 \cdot 2\text{THF}$ reactants are converted by vapour phase oxidation in the flame to SiO_2 and MgO , each in the form of a finely divided oxide soot. This soot mixture is collected on an alumina mandrel for examination, analysis and further treatment.

Analysis of the collected soot determines that a soot mixture consisting of 1.21% MgO and the remainder SiO_2 has been deposited on the mandrel. This soot mixture is consolidated by heating with a gas-oxygen flame to sinter the soot into a clear MgO-SiO_2 glass having a refractive index of about 1.460.

Example 8 - MgO-SiO_2 Opal Glass

The glass-forming procedure of Example 8 is repeated, except that argon carrier gas flow through the liquid $\text{Mg(hfa)}_2 \cdot 2\text{THF}$ reactant is increased to 720 cc/min., such that the soot mixture collected from the vapour phase oxidation of the reactant stream contains 7.74% MgO and the remainder SiO_2 by weight. This soot mixture is

-21-

sintered in a gas-oxygen flame as in Example 6 and the product is a dense, substantially void free MgO-SiO_2 opal glass.

5 In using β -diketonate complexes as sources of main group metals for vapour phase oxidation processes, it must be recognized that these complexes may undergo reactions at vapour delivery temperatures which may adversely affect the desirable vaporization and stability characteristics thereof. Reactions to be
10 considered which might reduce the volatility of the complex include electrophilic substitution of a halogen for a hydrogen atom on the β -diketone ligand, adduct formation by the complexing of the β -diketonate molecule with selected bases, replacement reactions wherein
15 a β -diketonate ligand is replaced by a halide and redistribution reactions wherein ligands are scrambled among various metal complexes to produce new complexes of low volatility. Avoidance of these reactions may require the use of delivery systems wherein each
20 vaporized reactant is separately transported to the reaction site for final mixing and vapour phase oxidation.

While the foregoing description has been primarily concerned with processes suitable for the formation of optically clear glasses useful, for example, in the
25 fabrication of glass optical waveguides, it will be appreciated that the present invention is applicable to the production of other pure unitary ceramic products, such as opal glass, semicrystalline glasses, or crystalline cermics, including porous glasses or
30 ceramics where only partial sintering of the oxide soot is permitted in the consolidation step. In addition, it is possible to process the oxide soot prior to consolidation if, for example, it is desired to shape the soot into a preform of a desired configuration.
35 This may be done, for example, by dispersing the soot

0103448

-22-

in a suitable vehicle and casting the dispersion into
a selected shape.

Claims:

1. A process for the production of a glass or ceramic article comprising a vapour phase oxidation wherein vaporized compounds are oxidized to form particulate oxide soot which is captured and consolidated to a unitary article by sintering, characterised in that at least one of the compounds is a β -diketonate complex of a metal selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table.
2. A process for the production of a glass optical waveguide comprising a vapour phase oxidation wherein compounds of selected metals are vaporized, the vapours are transported to an oxidation site, the vapours are oxidized at the site to form particulate metal oxide soot, the soot is captured and consolidated into clear glass and the glass is drawn into optical waveguide fibre, characterised in that at least one of the compounds is a β -diketonate complex of a metal selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table.
3. A process as claimed in claim 1 or claim 2 wherein the metal is selected from Li, Na, Be, Mg, Sc, Y, Cu, Hf, Zr, Ti, Zn, Cd, Al, Ga, Tl and Ce and wherein the β -diketonate complex has a vapour pressure of at least 10 mm Hg (13.34 millibars) at a temperature not exceeding 250°C.
4. A process as claimed in any of claims 1 to 3 wherein the β -diketonate complex comprises a β -diketonate ligand having a formula weight of at least 153.

-24-

5. A process as claimed in any of claims 1 to 4 wherein the β -diketonate ligand is derived from a fluorinated β -diketone. .

6. A process as claimed in any of claims 1 to 4 wherein the β -diketonate ligand is selected from (tfa), (hfa), (thd), (dfhd), (tod) and (fod) ligands.

7. A process as claimed in any of claims 1 to 6 wherein the β -diketonate complex is adducted with at least one Lewis base.

8. A process as claimed in claim 7 wherein the Lewis base is tetrahydrofuran.

9. A process as claimed in any of claims 1 to 8 wherein the particulate metal oxide soot is captured on a rotating mandrel.

10. A process as claimed in any of claims 1 to 9 wherein the captured soot is treated prior to or during consolidation to remove water, carbon and/or fluorine impurities therefrom.

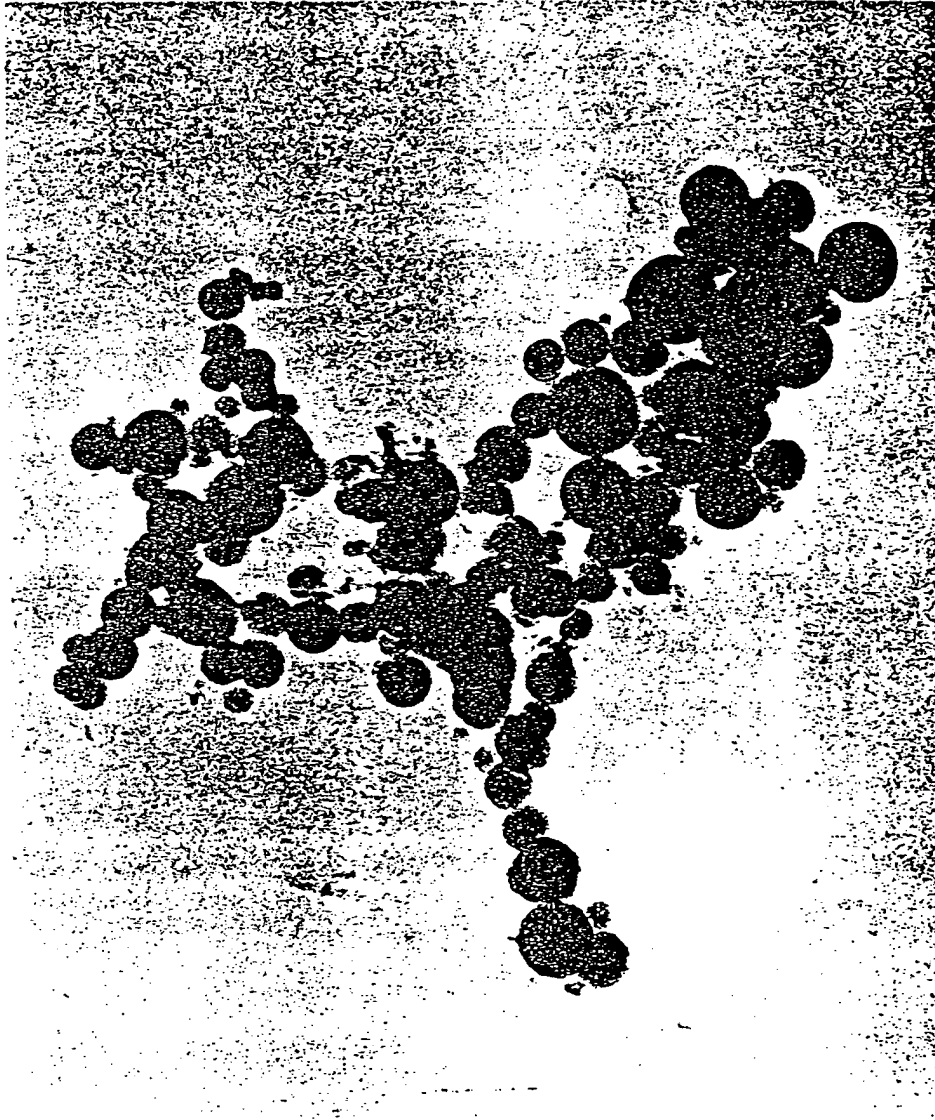
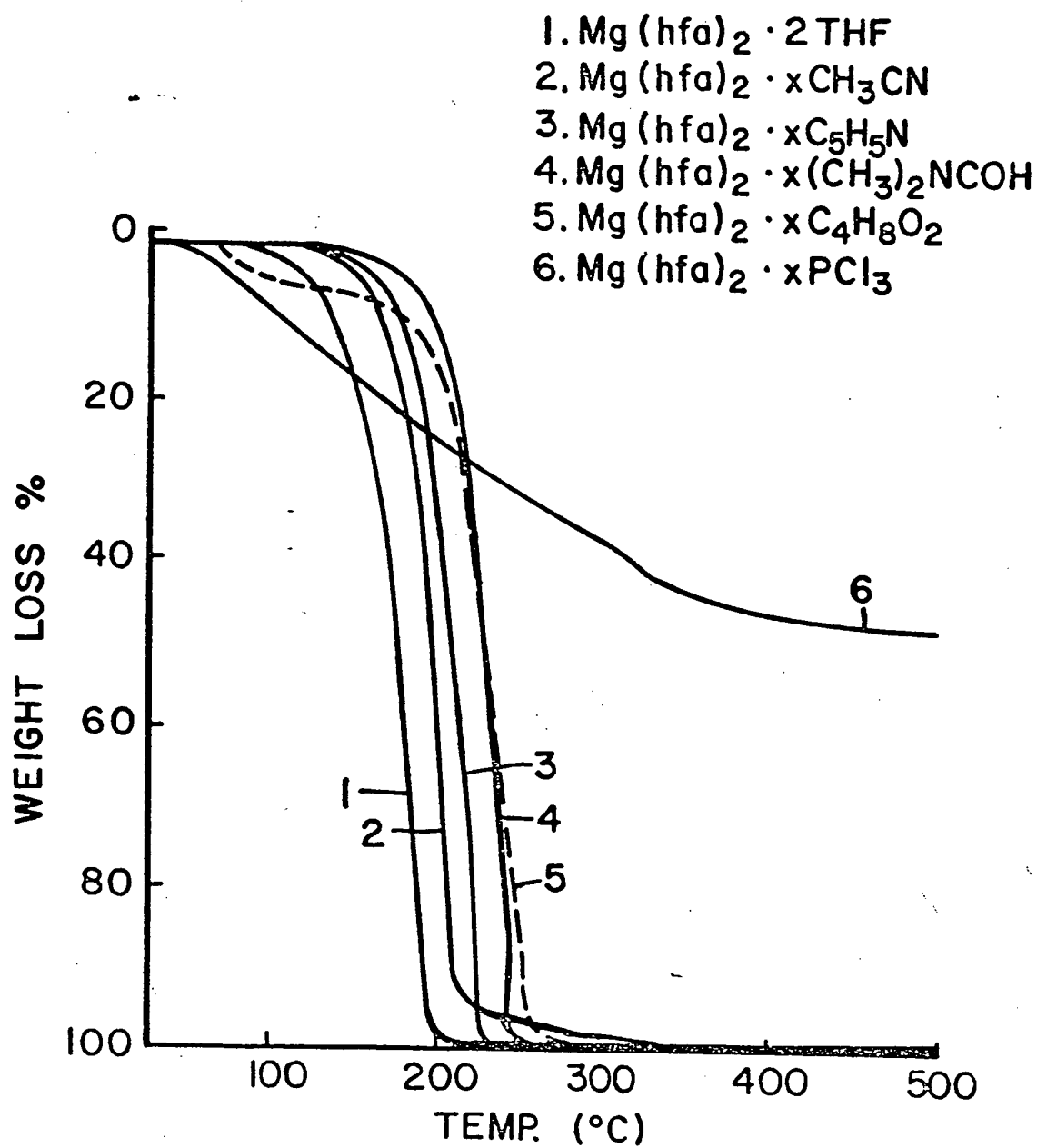


Fig. 4

*Fig. 3*

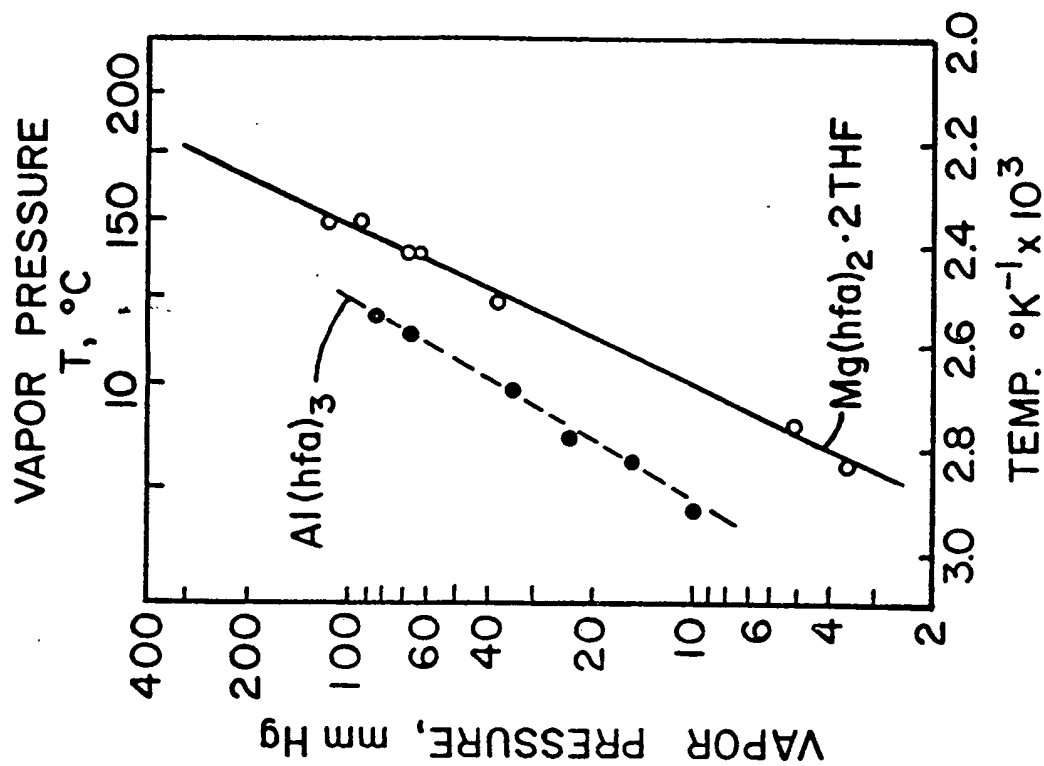


Fig. 2

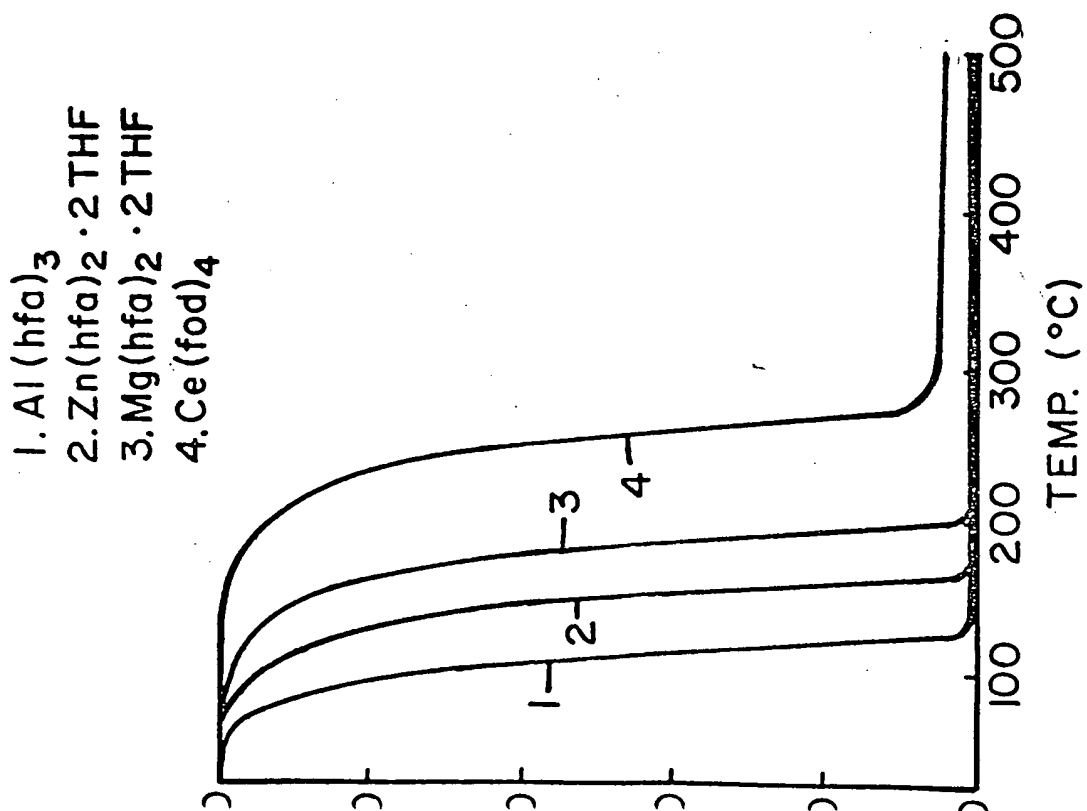


Fig. 1

-5- BASIC DOC.- C03C1/00

(19)



European Patent Office
Office européen des brevets

(11) Publication number:

0 103 448
A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 83305120.4

(22) Date of filing: 05.09.83

(51) Int. Cl.³: C 03 C 3/04
C 03 C 13/00, C 03 C 1/00
C 04 B 35/00



(30) Priority: 15.09.82 US 418215

(43) Date of publication of application:
21.03.84 Bulletin 84/12

(88) Date of deferred publication of search report: 10.10.84

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

diketone

(71) Applicant: Corning Glass Works
Houghton Park
Corning New York 14831(US)

(72) Inventor: Miller, Stephen Bruce
67 West Fourth Street
Corning New York 14830(US)

(72) Inventor: Stewart, Ronald Ieroy
741 Cardinal Lane
Big Flats New York(US)

(72) Inventor: Thompson, David Allen
1259 Stoneybrook Drive
Horseheads New York(US)

(74) Representative: Kyle, Diana et al,
ELKINGTON AND FIFE High Holborn House 52/54 High
Holborn
London WC1V 6SH(GB)

(54) Production of sintered glasses and ceramics.

(57) A process for the production of a glass or ceramic article comprising a vapour phase oxidation wherein vaporized compounds are oxidized to form particulate oxide soot which is captured and consolidated to a unitary article by sintering, characterised in that at least one of the compounds is a β -diketonate complex of a metal selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table is disclosed.

A process for the production of a glass optical waveguide comprising a vapour phase oxidation wherein compounds of selected metals are vaporized, the vapours are transported to an oxidation site, the vapours are oxidized at the site to form particulate metal oxide soot, the soot is captured and consolidated into clear glass and the glass is drawn into optical waveguide fibre, characterised in that at least one of the compounds is a β -diketonate complex of a metal selected from groups IA, IB, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table is also disclosed.

The present invention offers advantages over the prior art.



European Patent
Office

EUROPEAN SEARCH REPORT

0103448

Application number

EP 83 30 5120

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	THIN SOLID FILMS, vol. 41, no. 3, 15th March 1977, pages 247-259, Elsevier Sequoia S.A., NL; M. BALOG et al.: "Chemical vapor deposition and characterization of HfO ₂ films from organo-hafnium compounds" * Page 248, lines 4-11; page 249, paragraph 2.4; page 252, paragraph 3.1; page 253, paragraph 3.2 *	1,3-6	C 03 C 3/04 C 03 C 13/00 C 03 C 1/00 C 04 B 35/00
X	EP-A-0 055 459 (RIKUUN ELECTRIC) * Claims 1,3,5 *	1,3-6	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 03 B 37/025
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-06-1984	Examiner BOUTRUCHE J. P. E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding